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THE BLACKENED ROCKS OF THE NILE CATARACTS

AND OF

THE EGYPTIAN DESERTS

by

A. LUCAS

*Chief Chemist, Survey Department Laboratory, Cairo.*



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VIKAS J. CHOTWAT

# THE BLACKENED ROCKS OF THE NILE CATARACTS

## AND OF THE EGYPTIAN DESERTS.

The writer was led in the first instance to take up the study of this subject by having his attention drawn to some specimens of crystalline rock in the Cairo Geological Museum, which showed a peculiar black polished film on the outer surface.

Of the specimens one was a coarse-grained red granite (¹) from the First, or Aswan, Cataract of the Nile, and the others were a fine-grained red granite (¹), a basalt (¹) and a dolerite (²) respectively, all from the Second Cataract, above Wadi-Halfa.

Two visits were subsequently made to Aswan at a time of the year (³) when the river down-stream of the new dam was at its lowest level and when the rocks in the river channel were most exposed. Under these conditions the intense jet-black colour of the rocks forms one of the most noticeable features of the cataract area. The smaller rocks are entirely black, shine brilliantly, and have the general appearance of masses of coal or blocks of pitch, while the larger rocks show a broad band of polished black immediately above the water level.

This remarkable phenomenon has been commented on by many different writers and the following references may be quoted : — “The granite rocks at the Cataract of Aswan have a very thin, dark-black, shining surface-coating which gives them the appearance of having been pitched.” (⁴)

“Les rochers qui sont baignés une partie de l’année par les eaux du Nil sont quelquefois revêtus à leur extérieur d’une espèce d’enduit noir lisse et brillant.” (⁵)

“Lorsqu’on parcourt en barque les mille méandres de ces canaux profonds on est très frappé de la couleur d’un noir intense, ressemblant à un vernis que présentent ces rochers toujours immersés pendant

(¹) Collected by Sir William Willcocks.

(²) Collected by Dr. W. F. Hume, Egyptian Geological Survey.

(³) April 1904 and March 1905.

(⁴) RUSSEGGER quoted by Walther in “Die Denudation in der Wüste.” Leipzig, 1891, p. 453.

(⁵) DE ROZIERE, “Description de l’Egypte.” 2nd Edition. Tome XXI, Paris 1826, p. 242.

les hautes eaux. On croirait naviguer au milieu d'énormes entassements d'une houille très foncée et très luisante." (1)

" At the cataracts of the great rivers Orinoco, Nile and Congo, the syenitic rocks are coated by a black substance appearing as if they had been polished with plumbago." (2)

As will be seen from the last quotation this blackening of the rocks is not peculiar to the Nile; it is stated by Schweinfurth (3) to occur also on the Niger; it has been observed by Comstock at the rapids of the Tocantins river, Brazil, (4) and also in South America by Humboldt (5) and by Boussingault (6); by Pechuel-Lösche (7) on the Kiulu, and by Wissmann (8) on the Quige.

Darwin observed a similar phenomenon on the granitic rocks of the coast of Brazil near Bahia, though in this case the colour was brown and not black (9).

Specimens of garnetiferous gneiss (8) from the Third Cataract, and of a highly quartzose granite from a boulder found by the writer in the bed of the Nile at Shellal also show a brown and not a black film. In both these cases the rock is only slightly polished, and the browning is not limited to the surface but extends inwards for several millimetres.

Ball, describing a similar brown coloration on some specimens of syenite-porphry from Semna, writes : "The exposed surfaces are of a rusty brown; and where below the high Nile level, they are polished so as to give the rock the appearance of 'eisenkiesel.' The brown skin penetrates to a depth of about one centimetre, the limit between it and the normal grey rock being very sharply defined (9). "

One of the best specimens of a black film examined was from the inside of a stone water tank found on the top of Gebel Geili in the Sudan. This tank which is probably of ancient Egyptian date is made of dolerite and is only filled during the rainy season and then with rain water which only travels a very few yards before reaching the tank. The film which is a dense mat-black is found on the inner surface of the

(1) LORDET ET HUGOUNENQ. "Comptes Rendus." No. 19, (12 mai 1902).

(2) C. DARWIN. "Voyage of the Beagle." London 1901, p. 12.

(3) LORDET ET HUGOUNENQ. Quot. 1 in "Comptes Rendus." No. 19.

(4) T. B. COMSTOCK. Trans. American Institute of Mining Engineers, Lake Superior Meeting, Sept. 1904.

(5) A. VON HUMBOLDT. Quoted by Walther in "Die Denudation in der Wuste."

(6) M. BOUSSIGAULT. "Annales de Chemie et Physique". 5th Series, Tome XXVII, 1882, p. 289.

(7) Quoted by Walther in "Die Denudation in der Wuste."

(8) Collected by Dr. W. F. Hume, Egyptian Geological Survey.

(9) The Semna Cataract." DR. JOHN BALL. Quart. Journal Geological Society, 1903, Vol. LIX.

tank up to a height of about four feet, which is the height to which the tank is periodically filled. (¹)

All the films hitherto described have been on crystalline rocks, and it is on these rocks that the blackening ordinarily occurs. Two specimens, however, on limestone have recently been examined. One of these is from Ras-el-Kanais on the sea-coast west of Alexandria. The limestone here is soft and friable and the blackening occurs only about the tide mark, and neither below low-water nor above high-water level. Owing to the softness of the stone the surface of the rock is neither smoothed nor polished but very irregular, and there is no polishing on the film. (²)

The second specimen was from hard bands of nummulitic limestone outcropping and slightly projecting from the base of the cliffs about  $1\frac{1}{2}$  kilometres south-west of the village of Seraria, near Samalut, Upper Egypt. These beds of limestone are only separated from the river by a very narrow strip of cultivation and are probably under water every autumn except in years of very low flood. The film is black and polished. (³)

Having once remarked the blackened rocks of the cataract region at Aswan it is difficult not to notice also that many rocks away from the river have also a blackened surface. Thus the cliffs on either side of the valley that serves as a road between Aswan and Shellal, the limestone, sandstone and granite cliffs, respectively between Cairo and Korosko, that shut in the Nile valley, but do not come down to the water-edge, as well as many of the rocks and stones in the desert, are frequently brown or black on the upper surface.

This desert colouring has often been described. Zittel writes: "In the Libyan desert the upper surface of the light-coloured varieties of sandstone takes on a more or less intense brown colour, sometimes a complete black so that the Hammada (⁴) near Regenfeld (⁵) conveys the impression of being strewn with blocks of basalt or lava." (⁶)

Walther says: "As characteristic as the trace of the sand blast is the brown surface-colouring which is shown by many stones and rocks in

(¹) Sample collected and description furnished by T. Barron, F.G.S., Egyptian Geological Survey.

(²) Sample collected and description furnished by F. Hughes, Chemist, Khedivial Agricultural Society, Cairo.

(³) Sample collected and description furnished by H. J. L. Beadnell, F.G.S. Egyptian Geological Survey.

(⁴) The hard stony floor of the desert.

(⁵) South-west of Dakhla Oasis.

(⁶) "Palaeontographica," Vol. XXX. 3rd Edition. KARL A. ZITTEL, Cassel, 1883, p. 58-59.

the desert. The light-brown to dark-brown or even black colour is found on limestone as well as on siliceous rocks, it is formed in a relatively short time and must be regarded as a true desert appearance. (1)

Overweg and Wheeler are both quoted by Walther to the same effect. The former says: "Between the Wadi el Hessi and the Wadi el Shiati (south of the Tripolitan Hammada) is a region of pitch-black rock. The rock is a sandstone, in part permeated by iron ore and then completely black or brown, in part snow white and only on the surface exposed to the air covered with a thin shining crust. (2)

Wheeler, writing of the Californian desert says: "It is remarkable that over wide stretches, rocks and rolled material are coloured black on the upper surface just as though they were coated with a black varnish." (3)

Blake, referring also to the same desert regions of the south-west portion of the United States, says: "Travellers can hardly fail to note that most of the rocky outcrops of the harder rocks have a uniform prevailing blackness of the surface in strong contrast with the normal colour of the interior of the rock when freshly broken. (4)"

"The pebble-covered plains which extend over many hundred square miles in the northern arid regions of South Australia and in Central Australia," according to Moulden "present similar phenomena." (5)

Obrutschew mentions the occurrence of similar films in the deserts of Central Asia (6) and G. Linck describes films seen in the Nubian desert between Wadi-Halfa and Abu Hamed (7).

Captain Lyons, describing a layer of flints 8 to 12 feet deep that covers the limestone surface of the desert three hours west of Girga, Upper Egypt, mentions that "while the topmost layer is... blackened by exposure, the lower ones... usually... show no signs of blackening." (8)

Ball and Beadnell refer to a similar blackening noticed on their journey from the Nile valley to the Baharia Oasis, as follows: "The plateau rock... is a hard, white limestone. Just beyond the dunes this rock is very siliceous, the exposed surface showing a smoky black colour ; the

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(1) "Die Denudation in der Wüste." J. WALTHER, Leipzig, 1891 p. 453.

(2) Quoted by Walther in "Die Denudation in der Wüste."

(3) W. P. BLAKE. Trans. American Institute of Mining Engineers, Lake Superior Meeting, Sept. 1904.

(4) T. C. MOULDEN. Trans. American Institute of Mining Engineers, Lake Superior Meeting, Sep. 1904.

(5) Quoted by Von G. C. Du Bois in Tschermak's Min. u. Pet. Mittel, Vol. XXII, Section I, Vienna 1903.

(6) "Stratigraphy and Physiography of the Libyan Desert." CAPT. H. G. LYONS, R.E., Quart. Journ. Geol. Soc. Nov 1894.

rock is, however, quite white on fracture. The chalk forming the cliffs weathers in places to a smoky black colour." (1)

Du Bois, writing on films occurring at Surinam, in Dutch Guiana, summarizes most of the published references to similar phenomena. (2)

The above quotations will serve to show how universally distributed this colouring is in the desert.

There are therefore two classes of blackening: one of the rocks in the river channel and the other of the rocks and stones in the desert; and the first question that naturally presents itself is whether the two phenomena are identical, or if not identical, whether they have anything in common either in composition or mode of formation.

Walther is of opinion that the two are quite distinct, for he writes: "Certain black films which form on the banks (4) of tropical rivers should not be associated with the films of the desert as these latter are produced entirely without the aid of tropical climate or flowing water." (3)

"The appearances have fundamental differences and must not be confounded with one another." (5)

"The similar films formed on the banks (4) of tropical rivers are without significance in connection with the widely distributed phenomenon on the waterless desert. (6)"

With a view to discovering anything that might throw additional light on the composition or mode of formation of the river film, the rocks in the river channel at Aswan, Shellal and Kalabsha, and from Kalabsha to Korosko were carefully examined, and since it was thought possible that the desert blackening might have some bearing upon the question, many of the cliffs from Cairo to Korosko, near the river, but not actually washed by the water, were also inspected. The results of this examination will now be given in detail.

The rocks forming the cliffs of the Nile valley are mainly of three kinds namely limestone, sandstone and crystalline igneous rocks.

The limestone extends the whole distance between Cairo and Esna, a little south of which the sandstone begins, and at Silsila, some 70 kilometres before reaching Aswan, are the sandstone quarries used so largely by the ancient Egyptians.

The crystalline rocks which are first met with at Aswan extend as far as Shellal. Between Shellal and Kalabsha there are both sandstone and crystalline rocks, but at Kalabsha gorge the rocks are again wholly

(1) "Baharia Oasis." BALL and BEADNELL. Cairo, 1903, pp. 28 and 34.

(2) Von G. C. Du Bois, Tschermak's Min. u. Pet. Mittel Vol. XXII Section I, Vienna, 1903.

(3) "Die Denudation in der Wüste". J. WALThER, Leipzig, 1891 p. 458-461.

(4) i. e. rocky banks.

crystalline, after which all through Nubia until Wadi Halfa is reached there is nothing but sandstone. After the second cataract, however, in the schistose series near Akasha, marble bands are prominently developed similar bands being found also near the third and fourth cataracts. In the Amara cataract region the more prominent hills are composed of dolomite. <sup>(1)</sup> The rocks of the second and subsequent cataracts are crystalline.

#### DESERT FILM.

##### Limestone

At Helwan, near Cairo, the surfaces of the limestone hills are sombre and dark, which is due to the innumerable fragments of hard siliceous material splintered by weathering that cover the sides of the hills and the tops of the plateaux; all these fragments are more or less coloured, the colour varying from a light-brown to a deep-black. Any flints are also brown or black. These latter, however, are not very numerous except on the south-east side of the town where the sandy surface of the desert is in places strewn with flints and pieces of silicified wood which are all dark-coloured, the flints as a rule being quite black. Both the upper and under sides of the flints are coloured, but the coloration of the former is generally black, while that of the latter is sometimes only reddish-brown. Side by side with the flints are white quartz pebbles without any surface coloration whatever, and others of a very light yellow shade with only a trace of a coloured film.

The flints are all uniformly coloured on any one surface. This is also the case with the majority of the siliceous limestone fragments which are sometimes of a smoky grey colour and sometimes light brown but in other instances these fragments are partly brown and partly deep-black. Where the colour is uniform in tint the stone is uniform in composition, but where the stone is coloured unequally the black or darker coloured portions are harder and more siliceous than the rest. This peculiar patchy coloration has all the appearance of being a definite black layer several millimetres in thickness once existing as a vein in the rock and now partly exposed by the splitting and splintering action of the weather, but this, however, is not the case. There is certainly a vein of different material, but it is not black, being simply a layer of the limestone more siliceous than the rest, and it is the edges and the top of this harder layer that have blackened where exposed, and this blackening, although apparently extending into the interior of the stone, is merely a film on the surface.

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<sup>(1)</sup> Communicated by Dr. W. F. Hume, of the Egyptian Geological Survey.

The step pyramid at Saqqara, the three large and the various small pyramids of Giza, all show a well-defined browning of the outer surface. That part of the casing of the second pyramid which still remains is sensibly browner than the rest of the surface of the pyramid from which the coating has been removed.

Walther, referring to the great pyramid, writes: "The rock squares on the summit of the pyramid of Cheops show the beginning of the browning, as also the wide galleries at Tura, out of whose material the pyramids were built, and one finds to-day the brown films on surfaces which still carry the traces of the old Egyptian chisel marks." (1)

The material of the Saqqara pyramid is a yellowish, somewhat sandy limestone, while the limestone of the Giza pyramids is white and nummulitic. In some cases the nummulites have become quite black while the stone in which they are embedded is only brown. In the majority of cases, however, the nummulites and other fossils are a lighter shade than the rest of the stone.

Although the browning is more pronounced on the outside, it is present also on the less-exposed surfaces, as in the cracks and crevices between the stones, and even several metres down the open passages, such as that in the third pyramid at Giza.

In some cases the colour is largely removed by washing with water and a stiff brush, but in other instances such washing has very little effect. Very little sand or dust can be seen on the surface of the stones even when they are examined by the aid of a lens. The hard limestone of the pyramid plateau is generally of a cement colour with a brownish tint in places.

The cliffs at Thebes, although limestone, are by no means white even in the glare of the mid-day sun; the face of the cliffs is as a rule light-brown to reddish-brown, the tops and corner slopes dark-brown to black and the large boulders as well as the small stones and flints that strew the valley, are all more or less blackened on the outer surface. The light brown coating penetrates into all cracks and fissures and spaces between the bedding planes.

In places where there are mounds of earth and modern Arab dwellings at the foot of the cliffs, the face of the rock, when carefully examined, shows a certain amount of extraneous matter in fine particles adhering to the surface, more particularly in the crevices and depressions. This adherent material appears to be simply dust blown on to the surface from the remains of the mud huts forming the mounds: clayey matter,

(1) "Die Denudation in der Wüste" WALTHER Leipzig, 1891.

small sand grains and tiny particles of straw can all be detected. This dust can be readily removed by washing with water and a stiff brush, leaving the limestone white and unaltered underneath. The light-brown and reddish-brown coating can also be partly removed by washing; in some cases the original white stone is exposed below, in other cases small dendritic markings of manganese dioxide are found, while in many instances a slight reddish coloration still remains.

The boulders, which are very dark-coloured when seen from a distance, are found on closer examination to consist of a dense semi-crystalline limestone very different from that of the cliffs, and are not uniformly blackened even on the upper surface, but exhibit a sort of black excrescence in patches. This excrescence consists of fossils and flinty masses embedded in the limestone, and these have become blackened when exposed.

The greater number of the flints examined were light-coloured internally, some few, however, were dark, and many of both the light and dark varieties were coated on the outside with a white siliceous material.

On both light and dark-coloured specimens, and whether possessing the white siliceous covering or not, there is almost invariably a reddish-brown to black patina.

Walther says: "the well-known white decomposition rinds of flints do not colour either brown or black,"<sup>(1)</sup> but certainly in the case of the flints from Thebes, this does not hold true, and the blackening is very marked even where the "decomposition rind" exists; this is left white and unaltered when the coloured film is removed by acid.

**Sandstone.** The most remarkable feature of the Nubian sandstone from Kalabsha to Korosko as seen from the river is its dark-coloured upper surface. This is due to the fact that the tops of the cliffs are as a rule covered with a black or purplish-black layer sometimes two centimetres or more in thickness, the slopes and foot of the cliffs also being strewn with broken fragments of this same material. On the face of many of the cliffs there are dark-coloured bands of various degrees of thickness, together with round or oval black markings varying in size from a mere speck to about a centimetre in diameter. Some of the cliffs, as also some of the loose masses of rock at the bottom, show in addition a slight irregularly distributed black coloration which occurs in patches and which is never found uniformly covering the whole exposed surface of any one block.

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<sup>(1)</sup> "Die Denudation in der Wüste." J. WALThER, Leipzig, 1891 p. 453. 461.

One peculiar feature of the Nubian sandstone at Korosko is the great number of hard, more or less spherical, dark-coloured masses of various sizes that occur scattered about on the surface. These are the "volcanic bombs" (1) of Baker and the "black blisters which increase in size and form eventually round hollow black balls" (2) mentioned by Willcocks.

They are, however, simply concretions consisting of a sandstone core round which a thick mangano-ferruginous envelope has formed, and are not hollow in their original condition. The dark-coloured crust of the Nubian Sandstone is a hard, resistant ferruginous layer, containing varying amounts of oxide of manganese, which has been left exposed by the softer sandstone, which doubtless at one time covered it, having weathered away. It is in no sense a desert film, and the phenomena described by Zittel and Overweg already quoted (3) appear to be something quite different.

Some of the dark-coloured bands on the face of the cliff are of this same resistant layer, but others are much less definite, and contain a much smaller proportion of oxide of iron and more oxide of manganese: the small round and oval markings are also largely oxide of manganese. None of these are desert phenomena; the slight, irregularly distributed black coloration at the sides of the cliffs and on the loose blocks at their foot resembles very much a true desert blackening, and it is impossible to say definitely in every instance whether such is the case or not. It is believed, however, that in many instances it is no true desert film, but a slight accumulation of iron and manganese oxides that already existed in the sandstone, and has simply been exposed. In favour of this view is the fact that a similar coloration can be found in the joints between two separate blocks of stone even where the joint occurs at the back of the block.

The sandstone cliffs therefore from Kalabsha to Korosko along the river front, show no well-defined desert blackening such as that already described on the siliceous limestone and flints at Helwan, and on the fossils and flints in the limestone at Thebes. It is not stated that no such film exists on the Nubian sandstone, but merely that on the cliffs examined no instance could be found of a clearly marked, definite and unmistakeable desert coloration. The formation of such a film would naturally be precluded in those places where the thick, ferruginous crust exists, and where there is no crust the sandstone is so soft and friable that the surface would probably weather off before the film had time to form.

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(1) "Nile Tributaries of Abyssinia," SIR SAMUEL BAKER, London, 1872, p. 5

(2) "Egyptian Irrigation," SIR W. WILLCOCKS, 2nd Edition, 1899 p. 5

(3) pages 5 and 6.

**Crystalline  
Rocks**

The granite on the Aswan-Shellal road looks almost black when seen from a distance, which is partly due to a slight dull-black surface coloration of the granite, and partly to dykes of darker intruded rocks; these darker masses are as a rule split and cracked in every direction, and the small flakes and fragments that strew the slopes of the cliffs enhance the general dark aspect. The granite cliffs bordering the river at Shellal and Kalabsha, but far above any high-flood level of historic times, exhibit also more or less irregularly a slight dull-black surface, and in most cases, both here and on the cliffs of the Aswan-Shellal road, where this blackening exists, the granite is much disintegrated. The black coloration cannot be washed or brushed off.

**Summary**

**DESERT FILM.**—The several varieties of coloration on rocks and stones in the desert already described may now be briefly summarised : they are :—

(1) The black or purplish-black colour of the surface of much of the sandstone in Nubia on the cliffs near the river.

This is a hard, resistant mangano-ferruginous layer probably previously existing in the rock and now exposed on account of the softer sandstone once covering it having weathered away, and is in no way a desert film although frequently mistaken for such.

Even Zittel (<sup>1</sup>) does not seem to distinguish between the true film which is a mere patina on the surface of the stone and a distinct layer or crust which although similar in composition is very different in origin.

The composition is very variable; it is, however, essentially a mixture of iron and manganese oxides in varying proportions, but containing also other ingredients such as a silica, alumina, lime, etc.

The following is an analysis of such a layer examined by Wingard (<sup>1</sup>).

Manganese dioxide	...	...	...	...	30.57	%
Carbon dioxide	...	...	...	...	4.06	"
Barium monoxide	...	...	...	...	4.89	"
Alumina	...	...	...	...	8.91	"
Iron oxide	...	...	...	...	36.86	"
Silica	...	...	...	...	8.64	"
Water	...	...	...	...	5.90	"
Phosphoric acid	...	...	...	...	0.25	"
					99.88	"

(<sup>1</sup>) "Palaeontographica," K. A. ZITTEL. Vol. XXX 3rd Edition, Cassel, 1883 p. 58-59

(2) The brown coloration of the surface of the pyramids at Saqqara and Giza, of the limestone at Helwan and Thebes, and of the granite and other crystalline rocks on the desert cliffs near Aswan.

This is largely a genuine desert coloration, the colour being in great part cemented fast to the stones; in some cases, however, the colour is intensified by the presence of dust or other loosely adherent material.

(3) The brown to black coloration on flints and flinty material.

This is a genuine desert phenomenon and no part of the colour is in any way due to dust or dirt on the surface.

The composition and mode of formation of the desert film have been Composition  
and Mode of  
Formation dealt with at length by Walther.

Concerning the composition of the film he points out that almost all mixtures of iron and manganese oxides are found from the nearly pure iron oxide to the nearly pure manganese oxide and he records also the occurrence of traces of nickel found by Wheeler in some films from the Californian desert, 8% of cobalt found by Sickenberger in the Dakhla Oasis films, and 2.5% of phosphoric acid found by Piccard and Sickenberger in the films from some Egyptian limestones.

Concerning the formation of the film he writes:—

“ The brown protecting film is an appearance produced by the desert climate. It depends upon the action of the sun and a certain silica content of the rock. The colouring of manganese and iron is not derived from the rock, for if the latter were the case only rocks rich in manganese and iron would be brown, and it would be impossible for snow-white sandstone, limestone or flint to be coloured.” (1)

Wheeler, however, is quoted by this same writer to the opposite effect. Writing of the film on the rocks of the Californian desert, Wheeler says: “the manganese content of the rock appears to have taken part in its formation, for it is just the granites which have as a constituent an amethyst-coloured quartz which show the black coating most.” (1)

Walther accounts for the presence of iron and manganese compounds in the film by saying: “the clay dust which often fills the desert air and which is driven by the wind against all rocks, possibly contains manganese and iron and so may form the coloured salts.” (1)

In a later book Walther, explaining in detail the manner in which he believes the film to have been formed, writes: “the same forces come into play which in other rocks produce films of easily soluble salts, namely traces of rock humidity and intense sun heat”.

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(1) “Die Denudation in der Wüste.” J. WALThER, Leipzig, 1891, p. 453-461.

“ All the rocks in Egypt are more or less porous and take up a certain amount of water when moistened by dew or rain. All rocks in Egypt in addition contain traces of easily soluble salts especially common salt. These chloride solutions under certain conditions take up iron and manganese salts which were either already in the rock or have been blown on to the moist rocks in finest particles of dust.”<sup>(1)</sup>

“ The carbonic acid and phosphoric acid derived from the fossils also play their part as a means of solution.

“ When a rock which is permeated by such solutions is heated and dried the solutions are brought to the surface by capillary attraction and the iron and manganese salts dry and form a delicate covering.

“ The silica in crystalline rocks and the phosphoric acid in the limestones have such an affinity for freshly deposited iron and manganese oxides that at the place of contact chemical combination takes place which cements the oxides fast while the separated chlorides are blown away by the wind.”<sup>(1)</sup>

Merrill describes the film from some quartzitic boulders found in the Serrier desert in Utah as: “a thin dark varnish-like coating which consists largely of oxides of iron and manganese though a slight amount of organic matter is present.”<sup>(2)</sup>

Blake gives the composition of the film as oxide of iron or manganese or both, but makes no mention of any other constituent, and adds that: “in general ferrous salts are changed to the insoluble ferric form under the influence of the sun's rays,”<sup>(3)</sup> he states that “the coloration proceeds from within the rock rather than from without”<sup>(3)</sup> and ascribes its formation to “an osmotic flow, a kind of rock transpiration tending upwards and outwards to supply the excessive evaporation under hot arid conditions.”<sup>(3)</sup>

Blake states too, that the phenomenon is closely allied to the formation of caliche and to the incrustation of salt and of other saline soluble compounds generally called “alkali.” This view is also held by Sickenberger who writes: “as to the origin of the film the occurrence is the same as that so often seen in Egypt which brings about the formation of the salt crust and gypsum crystals of the sand-covered salines.”<sup>(4)</sup>

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(1) *Das Gesetz der Wüstenbildung.* J. WALTHER Berlin, 1900, p. 22-24.

(2) “*Rocks, Rock-Weathering and Soils,*” by J. P. MERRIL, New York, 1897, p. 256

(3) W. P. BLAKE. *Trans. American Institute of Mining Engineers, Lake Superior Meeting.* September 1904.

(4) *Manuscript report by Prof. E. SICKENBERGER kindly lent to the writer by Prof. Walther.*

Blake, however, finds difficulty with regard to the origin of the colouring on loose pebbles and says: "We should expect to find a greater diversity of colouring than actually exists if we consider the mass of the pebble alone as the source of the flow, and we would also expect to find a variation of colouring and of intensity corresponding to the varying degrees of hardness and of composition." (1) He states very definitely that "the mass of each pebble is not sufficient to yield an amount of colouring solution adequate to produce the change" (1) and to explain the formation of the film in such cases he assumes that "there is an osmotic flow from the subjacent earth to the pebbles, and that the solutions though small in volume and weak in composition are uniform in nature, and are finally concentrated at the exposed surfaces." (1)

Fraas states that in the formation of films weathering takes place from the centre of the rock, which becomes softer, towards the outside, which gradually becomes harder." (2)

Linck considers the films on desert rocks to be a product of chemical weathering which takes place under the special conditions consequent upon a tropical desert climate, and he divides the stages of the film formation into four phases, namely :—

- (1) Impregnation of the upper surface of the rock with dew.
- (2) Solution and decomposition of the rock minerals aided by the high desert temperature.
- (3) Oxidation of the solution by the help of various constituents of the air dissolved by the water.
- (4) Drying and crystallisation of the new formed combinations by means of the sun's heat. (2)

Obrutschew believes the film to be produced at the expense of the iron and silica content of the rocks. (2)

Du Bois is of opinion that there is some relation between the ozone content of the desert air and film formation, and he quotes Walther to the same effect (2).

The various quotations just given summarize all that can be found published concerning the composition and formation of the desert film.

With regard to the composition, most of the writers have omitted all mention of any constituents other than iron and manganese oxides ;

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(1) W. P. BLAKE. Trans. American Institute of Mining Engineers, Lake Superior Meeting, September, 1904.

(2) Quoted by Von G. C. Du Bois, Tschermake's Min. u. Pet. Mittel, Vol. XXII, Section I, Vienna, 1902.

nickel and cobalt however are each given once, and phosphoric acid is recorded on films from Egyptian limestone.

As to the origin of the film there are two main theories, namely that of Walther in which water in the form of dew or rain enters the rock, dissolves out sodium chloride, and in the case of limestone and fossils, also carbon dioxide and phosphoric acid, and then the solution thus formed, after further taking up iron and manganese compounds, either from the interior of the rock itself or from adherent particles of dust, is brought to the surface by capillary attraction and there evaporated, leaving the iron and manganese behind as insoluble oxides.

The second theory, that of Blake, apparently supposes that the iron and manganese salts are already in solution in the pores of the rock or in the ground immediately below, and are simply drawn to the surface and there evaporated, the solvent action of rain however not being wholly excluded.

Before being in a position to seriously discuss the question at all a more careful and detailed examination of specimens than had hitherto been attempted was necessary, and this was therefore made.

The film cannot be scraped or rubbed off in any way, but can be easily removed by means of strong hydrochloric acid in which it is readily soluble in the cold, forming a clear, dark-brown solution which becomes lighter coloured on heating.

Since the film cannot be separated mechanically and weighed it is difficult to determine its percentage composition. By adding together the weight of the various ingredients found and using this figure as the total weight of the film a percentage composition of some sort can be calculated, but this method assumes that everything present has been determined, and entirely ignores such a very probable constituent as water of hydration, which, owing to the nature of the sample, it is impossible to determine. To remove the film by acid and to weigh it by difference, although this has been the method followed in this laboratory, is not wholly satisfactory even with such a material as flint, and cannot be relied upon at all in the case of limestone, even though the limestone be siliceous.

However as no useful purpose was to be served by quantitative results, since the limits of variation are very wide, most of the analyses were qualitative only, in order to ascertain what constituents were present in each case and whether any substance could be detected in the film that did not occur in the rock underneath.

Several hundreds of films were examined altogether but the following tables summarizes the composition of the most typical:—

CONSTITUENTS	SILICEOUS LIMESTONE		FLINTS		Crystalline rock	Silicified wood
	Helwan	Thebes	Helwan	Thebes		
					Aswan	Helwan
Silica.....	nil	nil	nil	nil	nil	nil
Oxide of iron .....	present	present	present	present	present	present
Alumina.....	»	»	»	»	»	»
Oxide of manganese..	»	»	»	»	»	»
Lime.....	»	»	»	»	»	»
Magnesia.....	nil	nil	»	nil	nil	nil
Phosphoric acid.....	present	present	»	present	present	present
Sulphuric acid.....	»	»	»	nil	»	»
Potash .....	»	»	»	present	»	»

In addition to hydrochloric acid the action of nitric acid was also tried. With boiling nitric acid the solution is only slightly coloured, and in the cold usually not coloured at all. This apparently colourless solution, however, contains both iron and manganese compounds, as also does the solution produced by the boiling acid. All the other ingredients of the film are present also in each case.

The solubility of the film in water was next ascertained. After carefully washing the surface of a number of flints with water and a stiff brush and rinsing in distilled water they were boiled in distilled water for several hours then allowed to stand overnight, the water decanted off, evaporated to small bulk and tested. The solution thus obtained was quite colourless and neither iron nor manganese could be detected, but compounds of aluminium, calcium, magnesium, and potash, together with chloride, sulphate and phosphate were present.

An attempt was then made to determine these ingredients quantitatively in the water solution.

Two separate lots of flints were treated as described above, the details of the weight of the samples before and after treatment being as follows :—

	1	2
	grams	grams
Weight of flints before the action of water.....	871.7	872.5
Weight of flints after the action of water.....	871.5	872.3
Weight of material removed by the water .....	0.2	0.2

The samples, however, being too heavy for a delicate chemical balance could not be weighed with any great degree of accuracy.

In No. 1 the aluminium, calcium and magnesium were separately precipitated, but both the aluminium and magnesium were present in too small a quantity to be determined quantitatively ; the calcium, however, was weighed and found to amount to 5·04 % calculated as CaO.

In No. 2 it was found that the phosphate, sulphate, chloride and potash were each present in too small an amount to weigh.

The presence of phosphoric acid in most if not all films, and the occurrence of alumina, lime, magnesia, potash and sulphuric acid seems hitherto to have escaped notice.

The composition of the film having been determined, the origin of the constituents becomes the next problem.

Do the various ingredients forming the film come from within the rock itself or from without ? Walther says largely from within, but supplemented in certain cases by constituents derived from the desert dust. Walther's assumption, however, that "snow-white sandstone, limestone, and flint" never contain manganese, cannot be endorsed. There may be instances where such is the case, but in all samples of sandstone, limestone and flint examined in this laboratory, both iron and manganese have been found, though sometimes only in traces. Even some white quartz pebbles contained sufficient manganese to give a slight green colour when fused with oxidizing mixture.

Walther's conclusion therefore that the manganese and iron of the film cannot come from the rock itself is not endorsed by the experiments made.

Blake also says that usually the constituents of the film are derived from the rock, but that in the case of loose-lying pebbles the stones themselves do not contain sufficient of the colouring material necessary to produce the film, and then the earth immediately below furnishes

the requisite supply. No figures or data, however, are given to prove that the film even on small pebbles ever contains ingredients in greater quantity than could have been supplied from the stones themselves. In connection with this point three specimens of film-covered stone were well washed with water and a stiff brush, rinsed in distilled water, and again dried and weighed and then treated with acid. The weights of the stones before and after treatment and the weights of the films removed were as follows:—

NATURE OF SAMPLE	A FLINT	B FINE-GRAINED RED GRANITE	C SILICIFIED WOOD
	grams	grams	grams
Weight before treatment with acid .....	58.3474	348.00	136.2932
Weight after treatment with acid.	58.3130	347.75	136.2058
Weight of film removed by the acid .....	0.0344	0.25	0.0874

The phosphoric acid was then determined in these film solutions. Phosphoric acid was chosen because it is a characteristic ingredient and less likely to be so widely distributed as iron and manganese compounds. The following results were obtained:—

SAMPLE	A	B	C
	grams	grams	grams
Weight of $P_2O_5$ in film.....	0.00384	0.00223	0.00644
Percent. of $P_2O_5$ in film .....	% 11.12	% 0.89	% 14.73
Percent. of $P_2O_5$ calculated on original stone .....	% 0.006	% 0.0006	% 0.004

Although the percentage of the phosphoric acid in the film is high, the actual amount present is very small indeed, and represents only a trace when calculated as a percentage on the original stone.

Various other determinations of phosphoric acid were also made with the following results :—

SAMPLE	$P_2O_5$
Flint with slight brown film .....	% 0.03
Nummulite : no film .....	Trace
Flint with considerable black film .....	0.02
Interior only of flint.....	0.01
Interior of silicified wood.....	Trace

In none of the cases examined, therefore, can it be said that the phosphoric acid is in so large a quantity in the film that it could not have been derived wholly from the stone itself.

Merril<sup>(1)</sup> gives the following table showing the phosphoric acid content of various rocks :—

ROCK.	PHOSPHORIC ACID ( $P_2O_5$ )	
	MINIMUM	MAXIMUM
Granite .....	% 0.07	% 0.25
Diorite .....	0.18	1.06
Basalt .....	0.03	1.18
Limestone.....	0.06	10.00
Shale.....	0.02	0.25
Sandstone .....	0.00	0.1

With regard to the other constituents of the film the case is very similar, and in the hundreds of samples examined there was not a single instance of anything being found in the film that was not also present in the rock below.

(1) "Rocks, Rock-Weathering and Soils." G. P. MERRIL, New York, 1897, pp. 6-8.

In the case of the film upon flints, for example, all the ingredients composing the film are such as occur naturally in the flints themselves. The following analyses of flints may be quoted :—

**Flint.**

CONSTITUENTS	1	2	3	4	5
	EXTERIOR	INTERIOR	EXTERIOR	INTERIOR	INTERIOR
Silica .....	88.63	97.01	97.91	99.18	96.31
Alumina .....	..	..	..	..	0.30
Oxide of Iron .....	0.74	0.76	1.28	0.54	0.25
Lime .....	0.90	0.66	..	..	0.47
Potash .....	0.12	..	..	..	..
Soda .....	..	0.50	0.66	0.28	..
Phosphate of Lime.....	0.09	..	..	..	..
Carbonate of Lime.....	8.26	..	..	..	..
Carbonate of Magnesia ..	0.18	..	..	..	..
Water and Organic Matter.....	1.08	1.16	..	..	2.81
	100.00	100.09	99.85	100.00	100.14

These analyses, however, are all more or less incomplete, and although phosphoric acid is only given in one sample, and manganese is not mentioned at all, it is very probable indeed that traces at least of both these substances were present in every case. As already mentioned both manganese and phosphoric acid were found in all samples of Egyptian flints tested.

If, then, the film has originated wholly from within, to what is the decomposition of the rock due, and what has caused the separation and precipitation of the film constituents ?

(1) | VON DER MARCK. Quoted by Roth in "Allgemeine und Chemische Geologie," Berlin,

(2) | 1879, vol. I., p. 95.

(3) | FRISCH. Quoted by Roth in "Allgemeine und Chemische Geologie," Berlin, 1879.

(4) | vol. I., p. 95.

(5) RICCIARDI. Quoted by Roth in "Allgemeine und Chemische Geologie," Berlin, 1879 vol. II., p. 565.

The experiments of the Rogers Brothers in 1848,<sup>(1)</sup> of Richard Müller in 1877<sup>(2)</sup> and the more recent work of F. W. Clarke<sup>(3)</sup> all prove that even pure water partially decomposes many minerals and rocks. The Rogers Brothers and Müller also showed that the solvent action upon the rocks tested was much increased when the water contained carbon dioxide in solution.

Both these facts have been tested and confirmed in this laboratory, and the experiments will be described later.<sup>(4)</sup>

The amount of any given compound that will dissolve in water varies with the nature of the compound and the conditions under which solution takes place, increasing as a rule with increase of temperature, and increasing also when certain other bodies are present at the same time; the solubility of calcium sulphate for instance is much increased by the presence of sodium chloride, and that of calcium carbonate by the presence of either sodium chloride or sodium sulphate. Free phosphoric acid is also present, however, in a large number of cases, and this will materially aid any solvent action taking place. This phosphoric acid is derived from the decomposition of phosphates of iron, aluminium or calcium by means of water. On this action of water upon phosphates a considerable amount of work has been done from time to time and the results of this work have recently been summarized, and the work itself considerably extended by Cameron and Hurst<sup>(5)</sup> and Cameron and Seidell.<sup>(6)</sup>

"The phosphates of iron, aluminium and calcium are all substances which react with water or are hydrolyzed, yielding as one of the products of the reaction phosphoric acid and at the same time the hydroxide of the metal or possibly a basic phosphate. The solutions always contain free acid."<sup>(5)</sup>

The solutions thus formed are not, strictly speaking, solutions of the phosphates at all, but solutions of the decomposition products, and the phosphate itself is frequently present only in traces. The solubilities of ferric phosphate, aluminium phosphate and tri-calcium phosphate are all diminished by the presence of potassium chloride<sup>(5)</sup> and possibly therefore by sodium chloride also.

Carbon dioxide in the solution makes no appreciable difference in the extent to which ferric phosphate, aluminium phosphate or monocalcium

(1) American Journal of Science and Arts, 1818.

(2) Quoted in "Rocks, Rock-Weathering and Soils," by G.P. MERRIL, New York, 1897.

(3) Bulletin of the U.S. Geological Survey, No. 167.

(4) See page 36.

(5) Cameron and Hurst. Journal Amer. Chem. Soc., Vol. XXVI., No. 8.

(6) Cameron and Seidell. Journal Amer. Chem. Soc., Vol. XXVI., No. 11.

phosphate are soluble, but it increases the solubilities of both di-calcium and tri-calcium phosphate. (1) (2)

The temperature of the solutions, as would be expected, influences the solubilities of the various salts, and in each case a rise of temperature increases the solubility. (1) (2)

Not only, then, do all the film constituents occur in the rock or flint on which the film is found, but these constituents are all soluble to at least some slight extent in water, the solubility being increased in many instances by the presence of carbon dioxide, sodium chloride, phosphoric acid, etc.

Since in the case of limestone it appeared as though the coloration was darker where the rock was harder, several specimens were examined quantitatively for silica. The results obtained were:—

NATURE OF STONE	SILICA
	%
Fairly hard limestone from Helwan which only colours brown....	0.77
Very hard limestone from Helwan which colours black .....	21.25
Hard semi-crystalline limestone from Thebes which colours black.	59.50

This bears out Walther's statement that "the colour is much the darker the more the silica content of the rock." (3) Walther further says: "It is certain that the brown parts are harder and more resistant than the non-coloured parts, but it is doubtful whether this is cause or effect, the latter being thought to be the case." (3)

There can be little doubt, however, that the depth of the colour is dependent upon the amount of black oxide of manganese in the film, and that this is conditioned first by the manganese content of the rock, and secondly by the opportunities presented for the manganese salts to be brought to the surface and oxidized.

Du Bois believes that any chemical examination of the films must be unsatisfactory, first because the film is very thin and so intimately connected with the rock that it cannot be entirely separated, and secondly because some of the rock substance is likely to be included and so vitiate the analysis; he prefers, therefore, the microscopic examination of the films, and examined under the microscope sections of film-bearing laterites and other rocks from Surinam. (4)

(1) Cameron and Hurst. *Journal Amer. Chem. Soc.*, Vol. XXVI., No. 8.

(2) Cameron and Seidell. *Journal Amer. Chem. Soc.*, Vol. XXVI., No. 11.

(3) "Die Denudation in Der Wüste." J. WALThER. Leipzig, 1891.

(4) Von G. C. Du Bois. *Tschermake's Min. u. Pet. Mittel*, Vol. XXII., Section I., Vienna, 1903.

The results of this examination he gives in detail, and the conclusion arrived at was that although films are chiefly formed on decomposed rock yet they may also occur on rocks that are relatively undecomposed.

Before reading Du Bois' paper, sections had been prepared of various specimens of Egyptian desert films, including some from siliceous limestone, from flints and from crystalline rocks, and these had been examined microscopically. The results were similar to those obtained by Du Bois, and the conclusions were that although generally there was a certain amount of decomposition of the rock both throughout the interior as well as at the exterior edge, and more especially in the iron-containing minerals, yet no definite and regular alteration or decomposition of the rock from the centre towards the outside could be traced.

A more detailed microscopic examination of these specimens has been made by Dr. Hume of the Egyptian Geological Survey, and his note is attached as an appendix.

#### SUMMARY OF CONCLUSIONS.

The following are the conclusions arrived at :—

- (1) Since all rocks are more or less permeable to water,
- (2) and most rocks contain traces of iron, manganese, aluminium calcium, magnesium, potassium and sodium compounds,
- (3) and these compounds are all soluble to at least some slight extent in pure water, this solvent action being much increased by the presence of certain other substances such as carbon dioxide or phosphoric acid, and also by a relatively high temperature ;
- (4) that water in the form of occasional rain or of frequent and heavy dew or morning mist gains access to the rocks even in desert regions, and dissolves the various soluble constituents ;
- (5) that the solution thus formed is brought to the surface by capillary attraction, and that the water is there evaporated leaving the salts ;
- (6) that some of the salts, such as those of iron and manganese, are subject to further alteration at the surface, whereby insoluble oxides are formed ;
- (7) that a hot climate and small rainfall are necessary to the formation and preservation of the film.

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### RIVER FILM.

The limestone cliffs that for the most part enclose the Nile valley <sup>Limestone</sup> between Cairo and Esna do not come down to the river except in two or three places as for example near Samalut, at Gebel Abu Foda near Asiut, and at Gebel Haridi east of Tahta.

South of Esna, until past Wadi Halfa, no limestone occurs. The banks of the Blue Nile contain much limestone of an impure character, and similar deposits are also found in places on the White Nile.

As a rule the river film does not occur on limestone, probably because the stone is so soft that it wears away before the film has time to form. As already described, however, the limestone near Samalut which is hard and nummulitic shows the characteristic blackened and polished surface.

Between Esna and Aswan the sandstone only touches the river at <sup>Sandstone</sup> Silsila, and here there is no evidence of a river film.

From Shellal to Kalabsha, where the sandstone occurs in places, and from Kalabsha to Korosko, where there is nothing but sandstone, there is for the most part a narrow strip of cultivation between the cliffs and the river, and the sandstone only touches the water at very few points. At none of these places could any evidence of a river film be found.

Opposite Korosko there are rocks in the centre of the stream that are black and polished, and at first sight resemble very closely the film-coated rocks at Aswan. On closer examination, however, these rocks are found to consist of a hard, black, ferruginous sandstone brilliantly polished by the action of the river but bearing no trace whatever of a surface film. That the film, however, does exist on sandstone, is proved by its occurrence on the sandstone blocks of the old quay wall at Elephantine Island, as also on the neighbouring blocks forming the door, the staircase and the steps of the Nilometer.

The river film is practically limited to the area of the crystalline <sup>Crystalline</sup> <sup>rocks</sup> rocks ; it is very marked in the region of the first cataract, that is from Elephantine Island to Shellal ; it occurs, too, as already mentioned, at the second and third cataracts, and at the cataract of Kaibar (¹), and probably also at the remaining cataracts ; it is impartially distributed upon all varieties of crystalline rock.

(¹) *Des Cataractes du Nil.* Gotberg. Paris, 1867, p. 44.

Many of the crystalline rocks at the first cataract bear old Egyptian hieroglyphic inscriptions, and in some cases the incised portion of the writing is very much lighter-coloured than the rest of the stone, as though the cutting had been done after the formation of the film. There are inscriptions, however, on Elephantine Island and also on a group of rocks opposite on the Aswan side of the river in which the incised portion is as black as the rest of the stone.

As a general rule the rocks on which the films occur are hard and polished, and show no signs whatever of surface disintegration : there are cases, however, in which such disintegration exists, and the surface layer of the rock with the film on it has in these instances either already flaked off and fallen away, or is in process of doing so.

The height above the water of the upper edge of the blackened zone naturally varies with the height of the river which differs at different times of the year, but in many places it is well above any present day high flood level. Even upstream of the new dam with the reservoir full and the gauge recording 106 metres above sea level, although much of the blackening is under water, yet there are still rocks left exposed that show a metre or more of blackened surface, as for instance at Kalabsha gorge and on some of the small islands near Philae. (¹)

A special examination was made to ascertain whether the blackening extended below the lowest water level and existed on the rocks that are permanently submerged.

Walther, on the authority of Sickenberger, states that it does not. He writes: "Sickenberger found the dark black protecting film at the cataracts of Aswan and Kalabsha only at those points on the red, black and milk-white rocks which were at high flood level but never above the high flood zone, and just as little on the rocks which were always standing under water. (²)

At the time of a second visit to the Aswan barrage (³) the water coming through the sluices was confined as much as possible to the eastern side of the river in order that certain necessary masonry work might be executed below the dam on the opposite side. The water therefore in the western channels downstream of the dam was probably lower than it had ever been before in historical times. Even under these circumstances it was exceedingly difficult to ascertain whether the blackening did or did not occur below the lowest normal water level.

The whole exposed bed of the river immediately below the dam has

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(¹) April, 1904.

(²) "Gesetz des Wüstenbildung." J. WALTHER. Berlin, p. 22-24.

(³) March, 1905.

been so altered within the last few years by human agency that no certain evidence concerning its original condition could be obtained. Many of the rocks have been cut away to a considerable extent, while others have been built upon and obscured. Under these conditions it was found impossible to identify any of the exposed rocks and to say with certainty that any given rock was normally submerged and that its condition had not been altered since exposure.

Recourse therefore was had to the rocks still under water. Even here it was difficult to ascertain whether the submerged portion of any rock was blackened superficially or not owing to: (1) the turbidity of the water, (2) the fact that many of the rocks are naturally black, (3) that the rock just below the surface of the water is frequently covered with mud or a green slimy growth, or both. However, in several instances, more particularly in one case near the northern end of the navigation channel, there were found coarse-grained red granite rocks black and shiny for several metres above water level, at water mark covered with mud and green slime, and well below the water showing their natural red colour and no trace whatever of any surface discolouration. Similar rocks, black and polished above the water, but polished only and not blackened where submerged, were found also about half-way between the barrage and the town of Aswan.

Near Elephantine Island a narrow band of white just above the surface of the water was very noticeable on all the rocks. In the western channels near the dam where the water was unusually low, this white band was wider and a greater distance from the water; in several cases where measured it was found to be between 20 and 30 centimetres above the water level.

Samples of this white material were taken for analysis and its composition will be referred to later.

As seen from even a short distance the rocks in the river channel seem all equally black and polished, but on closer examination it is found that there is a great difference between one rock and another, and frequently also between various parts of the same rock.

Many of the rocks are of an intense jet black colour, but others, or in some cases, other faces of the same rock, although polished are hardly blackened at all, but merely brown; in some instances there is a vein or dyke of different material in the rock mass and this dyke has coloured differently to the rock itself, sometimes being blacker and sometimes less black than the original rock.

Although no evidence whatever could be found of the existence of the black film on rocks permanently submerged, the writer has examined

samples taken from below what is believed to be permanent low water level that do show the typical blackening. These samples were collected by a colleague<sup>(1)</sup> whose description is as follows:—

*Sample No. 3.*—“Granite from downstream of the dam. Had always been under water until the construction of the dam. Now it is exposed but covered at Nile flood.”

*Sample No. 4.*—“Granite from under the surface of the water and has until now never been out of water.”

On further reference to Mr. Morgan as to whether any mistake could have been made in taking these samples, he writes: “I can safely say that I stick by my first statements regarding the film-covered pieces of granite.”

Mr. Morgan further states that the rock on which the film was found below the water was bed-rock and not merely a large boulder that at one time had been out of water and had so acquired the film, and had subsequently fallen into the river and become submerged.<sup>(2)</sup>

**Chemical composition of the film.** In order to examine the film chemically it must first be detached from the rock, and since it cannot be rubbed or scraped off it is necessary to dissolve it off, which can be readily done, as in the case of the desert blackening, by means of strong hydrochloric acid.

It was advisable, however, to first of all clean the film from any extraneous matter that might possibly be adhering mechanically to the surface, such for instance as dirt or Nile mud. This was done by scrubbing with a hard brush and water and afterwards rinsing in distilled water.

The piece of rock was then placed film downwards in a porcelain dish containing cold concentrated hydrochloric acid where it was allowed to remain for several minutes; it was then removed and well washed with distilled water, the washings being added to the main solution.

The solution thus obtained was an intense dark-brown colour which on dilution was seen to contain a small amount of suspended matter; this was filtered off.

The clear dilute solution was evaporated to dryness and examined in the usual way.

Since the film cannot be separated from the rock in its unaltered state, but only after decomposition in acid, it cannot, therefore, be weighed, and so its percentage composition cannot be ascertained. To add together all the ingredients found on analysis, and then to calculate them as percentages with reference to their total weight, is inaccurate,

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(1) Mr. G. H. Morgan, Survey Department, Egypt.

(2) See Appendix II.

since carbon dioxide, combined water or other constituents impossible to determine, may be present in considerable amount and so vitiate the result. To determine the weight of the film by difference, as was done in the case of the desert flints, is not at all a satisfactory method when dealing with crystalline river rocks, since as a rule the sample is much larger than the ordinary flint and cannot be weighed on a delicate chemical balance. In order, therefore, to arrive at some idea of the relative proportions of the various ingredients present, as much of the film as possible was removed by means of acid from a known area, and the results obtained were calculated to a surface of one square metre. They were as follows:—

**Fine-grained hornblende granite**

CONSTITUENTS	GRAMS PER SQUARE METRE
Silica .....	1.42
Oxide of iron with a little alumina.....	3.66
Manganese dioxide.....	7.08
Lime.....	2.31
Magnesia .....	1.09
Potash .....	
Sulphur trioxide.....	
Phosphoric acid .....	
	Present, but not determined quantitatively.

The fact that the film contains other substances in addition to iron and manganese oxides seems hitherto to have escaped notice.

Darwin states that a film analysed by Berzelius "was found to consist of the oxides of iron and manganese." (1)

Lortet and Hugounenq say: "la roche est couverte d'une couche mince de bioxide de manganèse noir." (2)

After the film has been removed by acid a slight though distinct deposit of what looks like Nile mud can frequently be seen immediately underneath where the film has been, more especially in any depressions there may be on the surface of the rock. This deposit, which was never found on removing the desert film even from crystalline rocks, is seen on microscopic examination to be very quartzose in character and to very much resemble undoubted Nile mud from rocks in the same

(1) "The voyage of the Beagle." C. DARWIN, London, 1901, p. 12.

(2) "Comptes Rendus," No. 19, (12 mai, 1902).

locality, and it differs somewhat from particles of the rock itself scraped from a freshly-fractured surface ; the amount is too small to admit of chemical examination.

A very similar deposit was also found on removing the film from the sample of diorite taken from the Gebel Geili water-tank already mentioned.

In connection with this deposit below the film the occurrence of suspended matter in the acid solution of the film itself is of interest, since this was never noticed in the case of the desert films. This suspended matter is too small in amount to permit of detailed examination, but it appears to be very siliceous.

The presence of silica in the river films and its absence from the desert films is also noteworthy.

Some hundred or more different river films were examined altogether but in composition and general character they were all similar to the one already described. Phosphoric acid was present in every instance but seemed to be less marked than in many of the desert films.

The dense black film on the specimens of diorite taken from the water tank at Gebel Geili in the Sudan and already referred to differs somewhat from the ordinary film on the river rocks, not only on account of its denseness but also from the fact that the discolouration is not confined merely to the surface but visibly extends inwards for about two millimetres, and on most of the fractured faces this inward discolouration is brown and not black.

The blackening of the limestone from Ras el Kanais could not be examined satisfactorily owing to the nature of the stone on which the film occurs. It certainly resembles somewhat the ordinary river film and both iron and manganese were detected, although not present in more than traces ; this blackening, however, is not altogether free from the suspicion of being in part a vegetable growth.

The white deposit occurring above the water level on the rocks in the cataract area downstream of the dam was found on examination to contain lime, carbon dioxide, phosphoric acid and a trace of chloride.

The composition of the film having been determined, the source of ~~Mode of~~ ~~formation~~ the constituents and the reason of their separation and precipitation still remain to be ascertained.

All the ingredients composing the film are contained in the crystalline rocks on which the film is found.

The following analyses of these rocks may be quoted :—

**Crystalline rocks from Aswan.**

	1	2	3
Silica.....	69.95	68.18	70.25
Alumina.....	13.32	16.20	16.00
Ferric oxide .....	...	4.10	2.50
Ferrous oxide.....	4.90	...	...
Manganese oxide .....	...	trace	trace
Lime.....	1.79	1.75	1.60
Magnesia .....	0.66	0.48	}
Potash.....	3.47	6.48	
Soda .....	3.1	2.88	}
Water.....	1.27	...	
Loss on ignition .....	...	...	0.65
Titanium oxide .....	0.95	...	...
	99.62	100.07	100.00

(1) Hornblende Mica Granite from Aswan : analysed by Scheerer in 1866.

(2) Hornblende Mica Granite from Aswan : analysed by Wigner in 1878.

(3) Analysed by Delesse in 1851.

(4) Quoted by Grenville Cole in "Aides to Practical Geology," London, 1891, p. 199.

(5) Quoted by G.P. Merrill in "Rocks, Rock-weathering and Soils," New York, 1897, p. 66.

(6) Quoted by Persifer Frazer in Trans. Amer. Inst. Mining Engineers, Boston Meeting, 1883

Although these analyses make no mention of either sulphuric or phosphoric acids it was thought very probable that both occur, and so samples were specially examined for these two ingredients which were found to be present in every instance. All the constituents of

the film are present, too, in the river water both in suspension and in solution, as is shown by the following analyses :—

**Matter in suspension in Nile water.**

	1	2	3	4	5	6	7
	%	%	%	%	%	%	%
Insoluble matter and silica .....	58.17	48.07	55.09	58.22	49.38	53.04	50.37
Potash.....	0.68	0.98	1.82	1.06	trace	0.69	0.91
Soda.....	0.62	..	0.91	0.62	trace	2.16	2.52
Lime.....	3.31	4.08	2.06	3.18	..	2.25	2.63
Magnesia .....	2.42	0.81	1.12	0.99	..	0.66	3.42
Manganese oxide .....	0.09	..	..	..	..	..	..
Iron oxide .....	24.75	10.19	20.92	23.55	9.62	18.48	4.72
Alumina.....		19.08			13.60	8.76	21.90
Sulphuric acid .....	0.20	..	..	..	trace	..	..
Phosphoric acid.....	2.21	0.32	1.78	0.57	trace	..	0.24
Carbonic acid .....	1.55	1.47	1.28	1.44	..	..	1.66
Water.....	..	5.98	..	..	16.98	9.03	11.52
Organic matter.....	8.00	8.43	15.02	10.37			
Calcium carbonate.....	..	..	..	..	8.12	4.19	..
Magnesium carbonate.....	..	..	..	..	2.30	..	..
Calcium sulphate.....	..	..	..	..	..	0.75	..
Sodium chloride.....	..	..	..	..	..	0.04	..
Undetermined.....	..	0.59	..	..	..	..	0.11
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

(1) and (4) Analysed by Dr. W. C. Mackenzie, Journal Khedivial Agricultural Society, Cairo, Vol. I, pp. 102 and 135.

(2) and (5) Analysed by Dr. Letheby, Mins. Proceeds. Inst. Civil Engs., Vol. LX, p. 368. "The River Nile," by SIR B. BAKER.

(3) Analysed by Prof. E. Sickenerger. "La Configuration Géologique des Environs du Caire." Le Caire, 1890.

(6) Analysed by Mr. Brazier under Dr. Hofmann. Phil. Trans. Royal. Society, London, 1855.

(7) Quoted by Ventre Bey in "Sol Egyptien et Engrais," Bulletin Institut Egyptien, N°. 10, 1889.

**Matter in solution in Nile water.**

INGREDIENTS	MILLIGRAMS PER LITRE (PARTS PER MILLION)		
	1	2	3
Lime.....	44.22	51.78	42.1
Magnesia .....	10.30	10.29	...
Soda .....	5.87	13.01	...
Potash .....	15.01	4.04	9.1
Chlorine.....	6.28	17.37	...
Sulphuric acid .....	18.37	29.31	2.8
Phosphoric acid .....	trace	trace	trace
Nitric acid .....	trace	trace	...
Silica, etc.....	11.29	6.71	...
Organic matter.....	11.86	31.29	13.2
Carbonic acid and loss .....	42.81	40.91	34.1

(<sup>1</sup>) Analysed by Dr. Letheby, August 1874, Mins. Proceedings Inst. Civil Engineers Vol. LX p. 378, "The River Nile" by SIR B. BAKER.

(<sup>2</sup>) Analysed by Dr. Letheby, May 1875, Mins. Proceedings Inst. Civil Engineers, Vol. LX, p. 378, "The River Nile" by SIR B. BAKER.

(<sup>3</sup>) Analysed by Matthey Jan.-Feb. 1887, Bulletin No. 21, U.S. Department of Agriculture, 1903

Most of the analyses of Nile silt show the presence of all the ingredients of the film with the exception of manganese, and in only one instance is this recorded. There can be no doubt, however, that manganese is always present and that the analyses in which it is not given are incomplete in this particular, probably no search for it having been made.

The various ingredients of the film, with the exception of iron, alumina and manganese, are shown, too, as occurring in the Nile water. Since it seemed most probable however that both iron and alumina were also present, samples of the river water were examined and small amounts of both these ingredients were found in every case. Manganese was also found on special search being made. Two different samples of river water of about four litres each (<sup>1</sup>) after double and careful filtration were evaporated to dryness and the residue fused with oxidizing mixture, and in each case sufficient manganese was present to give a distinct green manganate.

(<sup>1</sup>) Taken at Cairo at the beginning of June 1904.

These statements so far will be generally accepted, but there seems room for a difference of opinion as to whether the iron, manganese and other compounds of the film originate from outside the rock on which the film is formed or from inside; whether in fact they have been brought by the water from a distance or whether they have simply come to the surface like an efflorescence from the rock immediately beneath.

Lortet and Hugounenq are of the latter opinion and write: "La couleur noire provient d'une décomposition et d'une oxydation particulières du silicate de manganèse contenu en certaine quantité dans les roches éruptives ainsi que dans le gres." (1)

"Le manganèse préexiste dans la pâte de la roche mais non à l'état de bioxyde." (1)

"Sous l'influence des conditions climatériques de ces régions — alternance des crues et les basses eaux, radiation solaire intense, absence de toute végétation saxophile — les silicates manganésifères des roches ont fourni par oxydation cette mince couche superficielle de manganèse qui donne à la surface polie et comme émaillée de ces granits et de ces porphyres leur étrange patine noire." (1).

This method of formation would be similar to that by means of which the desert films already described have been formed and the two phenomena would thus be identical. In support of this view the following arguments may be mentioned:—

(1) That all the constituents of the film are present in the rocks, and all rocks being more or less porous, water may penetrate not only through cracks and fissures and along bedding planes, but also through the capillary interstices between the various minerals, and, as already shown when dealing with the desert films, the constituents are all soluble to at least some slight extent in water, and more particularly in water such as the river water that contains carbon dioxide and various salts already in solution.

(2) That the various constituents once dissolved would come to the surface by capillary attraction when the time of high Nile was past and that particular part of the rock surface no longer submerged.

(3) That, therefore, all the conditions necessary for the formation of the film in a manner analogous to that suggested for the desert films actually exist.

To the contrary it may be urged that it is equally possible for the film constituents to have been deposited on the rocks

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(1) *Comptes Rendus*, No. 19, (12 mai 1902).

from the outside, and in support of this view there are the following facts :—

(i) That all the constituents occur in the river water both in suspension and in solution.

(ii) That although the films on various river rocks do show as already stated differences either of depth of colour or of colour itself yet these differences are not nearly so marked as in the case of the desert films, and if the film ingredients came from within the rock one would expect still greater differences, and that the river film, instead of covering granite, gneiss, dolerite, sandstone and limestone in exactly the same way and to almost the same extent, would vary considerably with the nature of the rock, and that more of the rocks in the river channel would be coloured brown, fewer black and some scarcely at all.

(iii) That the rock is polished below the film.

(iv) That there is evidence of the possible occurrence of Nile mud also underneath the film.

(v) That there is evidence of the possible occurrence of films on rocks permanently submerged and that this if proved would seem to preclude the possibility of its formation from within the rock, since as fast as the constituents were dissolved by the water and tended to come to the surface of the rock they would be carried away.

(vi) That the white material occurring as a narrow band on the rocks just above the water was found in places covering the film itself, and both its composition and mode of occurrence therefore point to its deposition from the water and not to its formation from the rock; hence a similar deposition of the film constituents would also seem quite possible.

(vii) That the microscopic examination of sections of the rocks on which the film occurs affords no conclusive evidence of any definite desintegration extending from the interior towards the surface such as might be expected if the constituents of the film came from the rock itself.

Loret and Hugounenq write: "Il ne faudrait pas voir dans le bioxyde de manganèse un sédiment apporté par les eaux ; s'il en était ainsi, tous les rochers baignés par le fleuve en aval de la cataracte devraient être également teints en noir : ce qui n'a pas lieu." (1)

This is plausible but fallacious, since it ignores the fact that on the Nile at least very few rocks occur in the river channel "en aval de la cataracte," and further that in one instance, namely that of the limestone near Samalut, already mentioned, the film is found outside

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(1) Comptes Rendus, n° 19 (12 mai, 1902).

the cataract area, and also that other necessary conditions, such as a high temperature may not be present elsewhere. It is a fact, however, that the film is chiefly found in cataract areas.

This is very noticeable in the Nile and is also mentioned by Darwin in connection with the film on the Orinoco; he writes: "it occurs on the rocks periodically washed by the flood and in those parts alone where the stream is rapid" (1) and he quotes the Indian saying that "the rocks are black where the waters are white." (1)

The explanation may simply be that it is only at cataract areas that the rocks are hard enough to resist erosion for a sufficiently long period to enable the film to form, since if the rock is soft and friable the surface is worn away too quickly to allow of the formation of the film.

On the whole the evidence is in favour of the film being formed from within the rock itself. Further proof of this is found in the occurrence of the film already alluded to inside the stone water-tank on Gebel Geili in the Sudan. Here there seems little room for doubt that the film constituents have all come from inside the rock, since no outside source seems possible.

In connection with the question of the solubilities of the chief constituents of the river film the following details may be mentioned. As already stated, pure water and especially water containing carbon dioxide in solution will decompose most rocks. To test whether this would hold good of the rocks forming the Nile banks the following experiments were made:—

Iron and manganese, the chief constituents of the film and those likely to occur in the rock in the most insoluble form, were alone taken into account in the experiments, and samples of Nubian sandstone and of coarse-grained red granite were powdered and a portion of each sample was placed in a stoppered flask containing distilled water and allowed to remain a month, being vigorously shaken at intervals during that time. The water was then decanted off, filtered and examined. Both solutions contained not only iron but traces of manganese also.

A further portion of the samples was treated in a similar way except that the water in the second case was saturated with carbon dioxide. These second solutions when examined after a month also contained iron and manganese.

Water either with or without carbon dioxide in solution will therefore extract not only iron but manganese also from both Nubian sandstone

and from the Aswan granite. The iron and manganese so extracted must necessarily be in solution as the respective bicarbonates.

The solubility of iron and manganese carbonates in pure water is however very slight, that of the latter being about one part in 8000 parts of water<sup>(1)</sup> but both dissolve more readily in water containing carbon dioxide in solution.

When dealing with the desert films it was taken for granted that the iron and manganese compounds became oxidized at the surface of the rock to the condition in which they are generally found, namely that of ferric oxide and manganese dioxide. The same action would seem to take place in the formation of the river film, but no explanation has been offered of what brings about this oxidation at any rate in the case of manganese.

The iron will probably, before its final oxidation, be present as ferrous bicarbonate, and the manganese as manganese bicarbonate. But both the iron and manganese exist in the film as oxides, so the question arises, what then has changed the soluble bicarbonates into insoluble oxides? All ferrous compounds in solution are very unstable and the bicarbonate is no exception, a solution of this salt being slowly decomposed by mere exposure to the air, and more rapidly by boiling, hydrated ferric oxide being precipitated.

With regard to manganese it is the "per" and not the "proto" salts generally that are unstable in solution, such salts as manganese sulphate or chloride being quite stable and not oxidized on exposure to the air. Manganese carbonate, however, is different; when freshly precipitated it is white, but exposed to the air while still moist, or if dried with free access of air, it turns brown, part of it becoming converted into hydrated mangano-manganic oxide.

In order to ascertain how the carbonate behaves when in solution, the powder, which was of a dirty brown colour and evidently contained some oxide, was placed in a flask with distilled water and carbon dioxide was passed through for about an hour. The liquid was then carefully filtered, the filtrate being clear and colourless. Since the most prominent conditions present at the cataracts are the agitation and aeration of the water, the effect of both agitation and aeration were tried on this solution, but after continued agitation, and after air had been blown through for several hours no change whatever was noticeable, the solution still remaining clear and without colour. Since it was possible that some of the salts naturally present in the river water might

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(1) "Treatise on Chemistry." ROSCOE and SCHORLEMMER. Vol. II, Part I, London 1899, p. 10.

be instrumental in bringing about the desired precipitation, the solution of manganous bicarbonate was mixed with Nile water, but again agitation and aeration were without effect.

On evaporating the solution over a water-bath a brownish precipitate of hydrated oxide quickly began to separate out.

On heating in a firmly-stoppered flask in the water-oven the hydrated oxide was again formed and in a comparatively short time.

On evaporation in the sun oxidation took place more slowly and a brown residue of the hydrated oxide was again left.

On heating the dry carbonate to a bright red heat in a gas muffle furnace for a short time it became converted into the brown mangano-manganic oxide ( $Mn_3O_4$ ) into which compound all oxides of manganese including the hydrated dioxide itself, are finally converted by ordinary strong ignition in the air. (1)

Forchhammer, however, found that manganous carbonate, when heated to  $260^\circ$  in an open vessel, is converted into dioxide, and on this reaction Charles Dunlop based his method for the recovery of manganese dioxide from the spent liquors of the chlorine still, a method that in 1857 was used commercially on a large scale by Charles Tennant and Co., of Glasgow. In this process the manganous chloride is first converted into carbonate by the action of carbonate of lime and the manganous carbonate so formed is then exposed to the action of a current of air for twenty four hours in an oven heated to about  $300^\circ$  which is always kept moist, when it is found that it becomes converted into a black powder containing 72 % of manganese dioxide. (2) (3)

The process now generally used, however, for the recovery of manganese dioxide is that invented in 1867 by Weldon, which depends upon the fact that manganous hydrate is completely transformed into dioxide by air heated to  $55^\circ$  when an excess of lime is present. The manganous chloride is first transformed into hydrate by the use of milk of lime which is added in excess of that required for the complete precipitation of the hydrate. A strong current of warm air is then blown through the mixture which transforms the greater part of the protoxide into dioxide. (2) (3)

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(1) "Treatise on Chemistry." ROSCOE and SCHOBLEMNER, Vol. II, Part II, p. 15, London, 1889.

(2) "Dictionary of Applied Chemistry," THORPE, Vol. I, p. 513, London, 1890.

(3) According to Dittmar the composition of the final product of heating the dioxide varies with the pressure of the oxygen and if this is greater than 26 atmosphere the product approximates more closely to  $Mn_2O_3$ . "Watt's Dictionary of Chemistry," Vol. III, p. 182.

According to the experiments of Wright and Luff on the effect of heating  $MnCO_3$  in air, unless the heating is continued for a long time and the temperature is kept very high the product contains more oxygen than  $Mn_3O_4$ . ("Watt's Dictionary of Chemistry," Vol. III, p. 182.)

Manganese dioxide can also be obtained by heating manganous nitrate.

Other methods by which manganese dioxide may be produced from solutions of manganous salts are those made use of in the laboratory, and are based upon the simultaneous oxidation and precipitation of a manganous salt. From the foregoing it is evident therefore that manganese dioxide can be formed from the carbonate or other manganous salts by purely chemical means.

In this connection a study of the comparatively recent discovery of the abundant deposits of oxides of manganese and iron over the floor of the deep sea becomes of interest.

“The hydrates of manganese along with ferric hydrate are among the most widely distributed bodies in marine deposits, being especially abundant in those of the abyssal regions. In the descriptions of the samples of the deposits from the various stations of the *Challenger* expedition, we have had to point out the presence of these oxides as thick or thin coatings on shells, corals, sharks' teeth, bones and fragments of rock. It may be said that manganese in this form exists in all deep-sea deposits, for rarely can a large sample of any mud, clay or ooze be examined with care without traces of the oxides of the metal being discovered either as coatings or minute grains.”<sup>(1)</sup>

“The numerous analyses.... prove that we have to do with a hydrated oxide of manganese mixed with various quantities of limonite, clay and other earthy and sandy matters.”<sup>(2)</sup>

The various opinions as to the mode of origin of manganese nodules in deep-sea deposits may be summarized as follows:—

1. The manganese of the nodule is chiefly derived from the decomposition of the more basic volcanic rocks and minerals with which the nodules are nearly always associated in deep-sea deposits. The manganese and iron of these rocks and minerals are at first transformed into carbonates and subsequently into oxides which, in depositing from solution in the watery ooze, take a concretionary form around various kinds of nuclei<sup>(3)</sup>.

This is the view generally accepted.

2. They are formed under the reducing influence of organic matters on the sulphates of sea water, sulphides being produced and subsequently oxidized<sup>(4)</sup>.

(1) “Voyage of H.M.S. Challenger,” Vol. VI, London, 1891, p. 341.

(2) Loc. cit., p. 366.

(3) MURRAY Proc. Roy. Soc. Edin. Vol. IX, pp. 255, 258, 1877 and Vol. XXIV, p. 529, 1876.

(4) BUCHANAN. Brit. Ass. Report. for 1881, pp. 583-4. BUCHANAN. Proc. Roy. Soc. Edin. Vol. XVIII, pp. 17-39.

This explanation was shown to be untenable by Irvine and Gibson who pointed out that sulphide of manganese could not be formed in this manner since it is readily decomposed by the action of carbonic acid whether free or loosely combined (¹).

3. They arise from the precipitation of manganese contained in the waters of submarine springs (²).

4. They are formed from the compounds of manganese dissolved in sea water in the form of bicarbonates and transformed at the surface of the sea into oxides which are precipitated in a permanent form on the bottom of the ocean (³) (⁴).

In connection with the various theories advanced to explain the deposition of oxides of manganese and iron on the floor of the ocean, the authors of the volume dealing with Deep Sea Deposits in the reports of the *Challenger* expedition, write : (⁵)

“It may be granted that the manganese in solution in the superficial layers and in the whole mass of the ocean might contribute a small part to the deposits of great depths; still, the bulk of the oxides of manganese in these deposits has evidently had another origin. The greater part of the manganese and iron of these deposits almost certainly comes directly along with clay from the alteration of the manganese and iron-bearing silicates scattered over the bed of the ocean and especially from those of volcanic origin.”

“.....we have shown that nearly all these rocks and minerals are decomposed or in process of alteration and that they nearly all contain protoxides of iron and manganese combined with silicic acid as for instance in augites, hornblendes, magnetite and the easily alterable basic volcanic glasses. It is known besides that sea water contains free or loosely combined carbonic acid furnished by the decomposition of organic substances or augmented in certain cases by gaseous emanation from submarine volcanic centres. Here all the conditions are favourable for the formation of manganese nodules. In the plastic materials of the broth-like ooze or clay we may picture the reactions that take place. The fragments of rocks and minerals yield earthy and alkaline carbonates which go into solution along with the carbonates of the protoxides of iron and manganese. The carbonates of the protoxides are in turn decomposed, absorbing and combining with oxygen in solution in sea

(¹) Proc. Roy. Soc. Edin. Vol. XVIII, pp. 54-59, 1891.

(²) Grubel. “Die am Grunde des Meeres vorkommenden Manganknollen” 1878 ii. pp. 189; 209.

(³) BOUSSINGAULT. “Annales de Chimie et de Physique,” 5 series Tom. XXVII, pp. 289. 311, 1882.

(⁴) DIEULAFAIT. “Comptes Rendus” Tome XCVI p. 718, 1883.

(⁵) “Voyage of H. M. S. Challenger,” Vol. VI “Deep Sea Deposits,” London, 1891, p. 374-5.

water; they are precipitated as sesquioxide of iron and peroxide of manganese in the mud, clay or ooze, whilst clay and precipitated silica represent the insoluble portion of the original minerals. The oozy surface layers of the deposit and the immediately superincumbent water must, from many indications, be regarded as the seat of these reactions."

Although this theory satisfactorily explains the formation of the oxides of iron and manganese in the deep sea it does not explain the occurrence of the very thin superficial coating of these same oxides on the rocks in tropical rivers. In this latter case there are no rock fragments or minerals slowly disintegrating in the undisturbed depths of the ocean where whatever is formed remains ready for further action or disintegration until at last the simpler insoluble oxides are deposited on the same spot where they are produced, but instead there is an always swiftly flowing and sometimes torrential river that at once carries away anything that may be broken from the rocks which everywhere present a smooth and rounded surface, brilliantly polished by the sand and fine mud that have swept past them for ages, and showing very few signs of disintegration or decay.

The second theory put forward to explain the formation of the deep sea deposits has been shown to be chemically impossible and hence cannot be true either of the blackened rocks in the Nile.

The third and fourth theories would seem to be similar to those held by Berzelius to account for the black film seen on the rocks of the Orinoco and Nile.

M. Boussingault says :

(<sup>1</sup>) "Ce célèbre chimiste pensait que les fleuves n'arrachent pas les oxydes au sol sur lequel ils coulent mais qu'ils les tirent de sources souterraines et les déposent ensuite sur les roches par une sorte de cimentation résultant d'une affinité particulière peut-être due à l'action de l'acide carbonique sur la potasse de feldspaths."

"On a vu que Berzélius attribuait le dépôt noir de la superficie des roches non pas à un sédiment mais à un produit dont les sources minérales seraient le véhicule parce qu'elles tiendraient en dissolution des carbonates qui se précipiteraient lorsque par l'agitation le gaz acide carbonique se dégagerait, les protoxydes de manganèse et de fer des carbonates dissous passeraient par l'effet de l'oxygène de l'atmosphère à un degré d'oxydation supérieur et se déposeraient sur le roches émergées."

Boussingault himself says very little about the origin of the soluble bicarbonates that finally give rise to the film of oxides but he

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(<sup>1</sup>) "Annales de Chimie et de Physique," 5 Ser. Tom. XXVII, pp. 293-296.

is in accord with Berzelius as to the mode of deposition. He writes:—

“Il est vraisemblable que là où se montre l’enduit noir de bioxide ou de sesquioxyde sur les corps submergés, sur les roches exposées alternativement à l’eau d’un fleuve et à l’atmosphère, le dissolvant des carbonates terreux et métalliques, le gaz acid carbonique a été expulsé par l’agitation et la dessication et que les sels de fer et de manganèse une fois isolés sont modifiés dans leur constitution produisant par l’action de l’air du sesquioxyde de rouge de fer et de l’oxyde manganique noir. (¹)

“La mer, les fleuves contiennent donc l’acide carbonique favorisant la dissolution des carbonates insolubles. Lorsque par une circonstance quelconque ce gaz est expulsé les sels sont précipités; les carbonates de protoxyde de fer et de protoxyde de manganèse une fois en contact soit avec l’oxygène de l’air, soit avec l’oxygène dissous dans l’eau sont modifiés dans leur constitution par la suroxydation de leurs bases; le carbonate de fer produit un sesquioxyde rouge; le carbonate de manganèse un b oxyde noir ou un sesquioxyde.

“C’est probablement à l’expulsion de l’acide carbonique que les granites de l’Orénoque, les syénites des bords de la Mer rouge, les roches cristallines du Congo, les assises calcaires ou dolomitiques des sources thermales, les concrétions formées dans les profondeurs de l’ocean doivent dans quelques circonstances l’enduit de manganèse qui recouvre leur surface. (¹)”

This method of accounting for the formation of manganese dioxide seems in theory quite satisfactory and simple, and a process that should take place readily, but in practice the expulsion of the carbon dioxide by agitation and, aeration failed as already explained, to produce any effect whatever and the most that could be done was to form the hydrated mangano-manganic oxide by heating.

What is required is the presence of some base with which the manganese dioxide can unite at the moment of formation otherwise it combines with the monoxide forming sesquioxide. Such a base is supplied in the Weldon recovery process by the lime, and it may possibly be under the combined influence of agitation, aeration and intense solar heat that some of the calcium bicarbonate that may be assumed to accompany the manganese salts (since all the films contain calcium compounds) may lose carbon dioxide and thus give rise to the base required, or the lime may be that formed by the simple solution in water of calcium phosphate as already mentioned. In either case the oxidation of the manganous salts to dioxide would then take place exactly as in the Weldon process.

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(¹) “Annales de Chimie et de Physique,” 5 Ser. Tome XXVII, pp. 306-311.

All explanations put forward, however, up to the present have simply asserted that such an oxidation of the bicarbonate to dioxide does take place without showing any adequate reason for this oxidation. Thus Campbell Brown in a recent paper says :—

(<sup>1</sup>) "Water containing traces of manganese salts forms by oxidation small concretions of dioxide and mixed oxides" and again : "The deposition of manganese dioxide is ... the result of oxidation by the oxygen dissolved in the water."

There is, however, another mode of formation of the manganese dioxide that has not yet been mentioned, namely, that by means of organisms. From time to time thick deposits containing manganese and iron have appeared in the pipes conveying various city water supplies. Thus considerable trouble was caused in Berlin in 1878, in Rotterdam in 1887, and since that time in other towns both in Europe and in America.

These deposits are usually attributed to various species of *Crenothrix* such as *Crenothrix Kuhniana*, *C. ochracea*, *C. polyospora*, *C. mangnifera*, etc., the last named being responsible for the deposition of oxides of manganese.

The iron and manganese oxides precipitated by means of the organisms are not merely superficial coatings which never grow thicker, but invariably distinct deposits sometimes 10 to 12 millimetres or more in thickness, which on analysis are found to contain considerable quantities of organic matter, amounting frequently to one third the weight of the dried deposit and consisting chiefly of what has been the living portion of the organism. (<sup>2</sup>) and (<sup>3</sup>)

It is believed, however, that the deposit of iron and manganese oxides on the rocks in the cataract areas of the Nile is not due to bacterial action, although the writer has been informed by Dr. Armand Ruffer that in connection with some experiments on this very subject he obtained a certain amount of evidence for the existence of manganeseiferous organisms in the Nile water. The reasons for this opinion are, first, the film apparently never thickens but always remains the same mere patina on the surface of the rock; secondly that the film contains little or no organic matter, no slime and no remains of organisms; thirdly, that the conditions that favour the growth of the various species of *Crenothrix* are lack of oxygen, absence of light and presence

(<sup>1</sup>) Minute of Proceedings of the Inst. of Civil Engineers, Vol. CLVI Session 1903, Part II, pp. 12 and 15.

(<sup>2</sup>) CAMPBELL BROWN. Min. Proc. of The Inst. of C. E. Vol. CLVI Part. II p. 17

(<sup>3</sup>) O. D. JACKSON. Journal Soc. Chem. Ind. May 31, 1902 p. 682.

of carbonic acid, none of which conditions hold where the film is formed; and fourthly, a very similar film is found on flints, etc., in the desert, where rain is almost unknown, and water, except for frequent and heavy dew, is entirely absent and where the heat of the sun is sufficient to kill almost all known forms even of bacterial life.

So far the possible formation of the film by chemical and bacterial means only has been dealt with; the operation of purely physical agencies will now be considered.

Beilby, in a recent lecture on "The Surface Structure of Solids,"<sup>(1)</sup> shows that "the operations of cutting, filing, grinding or polishing produce on the surface of solids a thin film which is in many respects essentially different from the general body underneath it," and that "this surface film results from a certain mobility which is conferred on a thin layer of molecules by the tool or polishing agent moving over the surface" and "while it is in the mobile condition the film of solid molecules behaves like a liquid and is subject to the action of surface tension." Although Beilby worked chiefly with metals he gives one instance of the formation of a film upon calc spar and one of a film upon glass, and in summing up says: "glass agate, calc spar, graphite, metals of all kinds, salts of all kinds, gelatine and cellulose, all appear to flow in the same way."

Fascinating as would be the solution of the problem under discussion along the lines now mentioned there seems no evidence whatever that the river film is formed in any such manner. In the first place the film not only differs in structure from the rock underneath, but it also differs in composition and no matter what the nature of the rock may be, whether granite, gneiss, dolorite or sandstone, the constituents of the film are always the same. In the second place the rock is polished below the film and when the polished film is removed the second and underneath polish on the rock remains.

A molecular disturbance of the surface of the rock resulting in the surface molecules acquiring a certain freedom of movement and rearranging themselves under the action of surface tension while in the mobile condition is probably, however, the cause of the polish on the rock the polishing agent being sand grains in the river silt.

This explanation is in accord with Lord Rayleigh's remarks in his lecture on "Polish" quoted by Beilby, that "one is inevitably led to the conclusion that in all probability the operation is a molecular one."

Any such molecular disturbance, however, would be so very superficial that the aggregating at the surface of the comparatively large amounts of iron and manganese compounds found in the film cannot be satisfactorily accounted for in this way.

Although the researches of Spring, Guthrie and Roberts-Austen prove that molecules of solids are not in a state of rest but possess a certain amount of mobility that enables dry and solid elements to interpenetrate each other, yet there is nothing to suggest that the constituents of the black river-film have come to the surface by any process such as migration in the solid form from the interior of the rock. The film covers not only the different minerals in a single rock such as the quartz, felspar and mica in a granite, but covers also widely different rocks as for instance sandstone and basalt, and it is hardly conceivable that similar migration of the same compounds could have taken place in all these different cases simultaneously and practically to the same extent.

Any formation of the film from the rock itself by purely physical means seems to be entirely out of the question.

One of the most noticeable features of the film is its extreme thinness: it is so thin that it cannot be measured, and never seems to vary or to increase in thickness, but wherever found it is apparently always the same.

Boussingault says: "L'épaisseur ne dépassait pas 0.1 de millimetre (1)." Humbold, however, gives the thickness as less than 0.01 of a line which is more in accord with the writer's experience.

#### SUMMARY.

The following are the conclusions arrived at with regard to the formation of the river film :—

(1) The evidence as to whether the film constituents originate from within the rock on which the film is formed or are deposited by the river from outside, is not conclusive either way.

(2) Reasoning by analogy, however, the probabilities are that the river film is formed in an exactly similar manner to the desert film, namely from inside the rock.

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(1) "Annales de Chimie et de Physique." 5th Series, Tome XXVII 1882 p. 289.

The foregoing study of the composition of these films makes it abundantly clear that a comparatively large amount of purely chemical disintegration of rocks occurs in the Egyptian desert, and that probably this chemical disintegration of rocks in dry and tropical climates is considerably greater than is usually supposed.

It is clear also that phosphoric acid is much more widely prevalent as a rock constituent than is generally stated to be the case.

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## **APPENDICES.**



APPENDIX I.

LIST OF ROCK SPECIMENS FROM WHICH SECTIONS WERE MADE

No. OF SLIDE.	SPECIMEN
1	Flint from Helwan with film. No white siliceous coating under film.
2	Flint from Helwan with film. White siliceous coating under film.
3	Flint from Thebes with film. White siliceous coating under film.
4	Sandstone with discoloration from surface of plateau, Wadi Hillal, Mahamid, near Edfu.
5	Limestone from Giza with brown film.
6	Coarse-grained red granite with flakes of biotite from Aswan : brownish-black desert film.
7	Fine-grained granite with mica in patches from Aswan : black river film.
8	Granite approaching syenite from Aswan : brown desert film.
9	Fine-grained, friable red granite with gneissose aspect from Aswan : black desert film.
10	Granite similar to No. 8 probably dyke intruding into No. 11 ; from Aswan : black river film.
11	Biotite gneiss from Aswan : black river film.
12	Hornblende diorite from second cataract : film removed by acid.
13	Fine-grained, red granite from Aswan : black river film.
14	Porphyritic orthoclase felspar granite from Aswan : slight polished river film.
15	Fine-grained, red granite from Aswan : black river film.
16	Fine-grained, red granite from Aswan : brown-black river film.



## DETAILED DESCRIPTION OF SLIDES.

BY DR. W. F. HUME, GEOLOGICAL SURVEY, EGYPT.

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SLIDE No. 1.—Consists essentially of silica of chalcedonic nature forming a compact dark-brown mass through which are scattered minute grains, obviously the remains of a glauconitic material originally deposited in the internal chambers of foraminifera. In places these have preserved their true relations, the form of a rotalia being distinctly outlined. There is a faint yellow-brown tinting near the border which may be due to iron compounds derived from the glauconitic material. One shell in the slide is filled with well-marked chalcedony. Part of the iron salts for the film could well have been derived from the glauconite, which is abundant. There is perhaps a slight tendency to concentration near the border.

SLIDE No. 2. —Differs markedly from the preceding, consisting of carbonate of lime (showing the characteristic iridescent polarization tints) and chalcedony in about equal proportions. Rounded grains of glauconite are also present, but very rare. Under a lens the rock shows numerous cross sections of foraminifera, and silicification has taken place specially in the interior of their chambers. Along one small edge there is marked enriching in glauconitic material ; but the slide does not appear to have secured the film. In the hand specimen five stages are recognizable, these are from outward inwards. 1. The dark border. 2. A white chalcedonic looking layer. 3. A yellow decomposition band nearly 1 mm. thick. 4. In places a less-marked dull band separates this from the main flint.

SLIDE No. 3.—This specimen has an important bearing on the preceding one, as it has films preserved on both surfaces. Though unfortunately rather fine-grained, several stages can be recognised. In the first place in the kernel of the "flint" the most conspicuous member is the carbonate of lime, but wherever fossils occur in the mass, there is one marked feature, namely the aggregation in those neighbourhoods of the small granules, which by analogy, are regarded as glauconitic. Higher powers

than a  $\frac{1}{8}$ th. (the one used) are needed to show whether there is silica aggregation as well.

The white film on one side is of much interest on account of its marked separation from the limestone matrix. It consists entirely of chalcedony and large grains of glauconite, the latter being distributed freely throughout the chalcedonic groundmass. The same holds good for the opposite edge, but in this case the chalcedony has broken into the limestone in vein form, the latter being broken up into islands surrounded by siliceous material. The brown grains are also closely connected with the chalcedony of this border.

SLIDE No. 4.—The rock is essentially a mosaic of quartz fragments but three other constituents are recognisable. 1. A thin cement of carbonate of lime round some of the grains to which is due the slight effervescence of the rock in acid. 2. Highly refracting brown crystals with high refractive index, in all probability crystals of rutile (titanium oxide) and 3. A dull whitish-green amorphous substance, which from its general appearance and occasional circular form recalls the "glauconite" deposits in the chambers of organisms.

Neither in the hand specimen nor in the slide is there evidence of a gradual change from within outwards, the darkening being absolutely superficial.

SLIDE No. 5.—There is no evidence of film, the rock being entirely carbonate of lime with cavities.

SLIDE No. 6.—Coarse-grained red granite with flakes of biotite and brownish-black desert film. The rock has obviously undergone a large amount of strain, the quartz being in mosaic form, and the felspar being a microcline felspar showing the most striking lattice and cross-hatching structures. In places there is a marked microgranophytic structure. Biotite mica occurs as rare yellow-brown strips but there is no indication of the concentration of any of the minerals towards the film edge, which is not itself represented in the section.

SLIDE No. 7.—Rock essentially a fine-grained granite consisting of quartz with more or less wavy outlines and well-developed microcline felspar. There are a few patches of brown mica, but the rock itself shows very little alteration, and there is no evidence of any special change at the edges; the film itself is not shown.

SLIDE No. 8.—This rock in the hand specimen resembling a syenite, in the slide is seen to be a gneiss closely related to No. 7. The quartz crystals are broken up into a mosaic of irregularly outlined grains, the cross-hatch structure of the microcline is well developed, and the mica, which is of a green colour, is broken into fragments, which tend to run in long foliation lines across the slide. Here also there is no evidence of any concentration of altered material at the edges; the film itself is not represented. There is a certain amount of decomposing felspar irregularly scattered.

SLIDE No. 9.—Has a resemblance to the preceding as regards the character of the quartz and the drawing out of the mica, though this character is less evident than in No. 8. The predominant felspar is not, however, the clear microcline with marked cross-hatching, but a very kaolinized felspar having the relations of orthoclase. There are indications that the microcline is derived from the orthoclastic potash felspar. There is a marked absence of distinct ferriferous constituents in this and the preceding slide, and no observable differences near the edge.

SLIDE No. 10.—Belongs to the same series as above, the mineral constituents being the same; it seems to have undergone less crushing, the quartz crystals being more distinct and the microcline scattered. The micas are all orientated in the same direction, suggesting gneissose structure.

SLIDE No. 11.—A biotite gneiss in which the quartz mosaic is well developed. There is a large amount of decomposing felspar associated with the quartz, but most of the clearer grains show plagioclastic twinning. The straw-yellow mica is orientated parallel to the direction of foliation.

SLIDE No. 12. -- A hornblende diorite in an advanced stage of decomposition. The felspar has lost all traces of twinning, and the alteration products appear to be carbonate of lime or various forms of lime silicates. The hornblende is less decomposed, the  $124^{\circ}$  cleavage being well-marked in many of the cross-sections, which are largely of faint yellow-green colour. There is a notable difference here when compared with the previously described rock, the felspar having undergone intensive decomposition near the smooth polished edge, but the film is unfortunately absent.

SLIDE No. 13.—A member of the crushed quartz-microcline granites with green mica and a highly altered felspar. The description for such slides as No. 8 applies here, except that the altered felspar is more abundant, the stage of crushing to which this rock has been submitted being probably less than that undergone by No. 8. No concentration of decomposition products near border.

SLIDE No. 14.—Granite, which represents the first step in the series of which No. 8 and 13 are members. The main features are the large and uncrushed condition of the quartz, the porphyritic and unaltered character of the orthoclase felspar, the biotite mica is in its original condition, but the presence of some microcline shows that the crushing stage is just beginning. A few ferruginous constituents showing whitish alteration products by reflected light (? titanoferrite) are also present. No definite arrangement of materials near any border.

SLIDE No. 15.—This granite agrees with the above in the presence of microcline, but markedly differs from it in fineness of grain, in the great abundance of a felspar which in its central parts has undergone intense local decomposition to muscovite but around which is a fresh zone. The felspar shows orthoclastic twinning (Carlsbad). The mica is irregularly distributed, and as is usual with the granites, there is no concentration of decomposition products. There is one small portion showing good granophyric structure, the quartz and felspar being intergrown in striking manner.

SLIDE No. 16.—Appears to be intermediate between Nos. 14 and 15 as regards decomposition of the felspars, there being some decomposed orthoclase felspar, a notable abundance of clear microcline, and some good granophyric structure. The biotite is irregularly distributed.

#### SUMMARY OF RESULTS.

From the above results it will be seen:—

- (1) That as regards the flints there is a general tendency to the presence of chalcedony and an increase in the amount of glauconitic or phosphatic materials (obviously internal casts of organisms) towards the film border.
- (2) In the sandstone evidence of any change outwards is absent.
- (3) The same holds true for the limestone, there being no evidence of any change outwards.

(4) The group of granites examined are at various stages of decomposition and strain, but there is no evidence that film structure is in any way dependent on the alteration as indicated by the felspars, and there is no concentration of the white alteration products towards the border.

(5) The same holds good for the gneiss.

(6) In the dolerite there is a very marked increase of white decomposition products of felspathic origin towards the film border.

In the flints and dolerite, therefore, the microscopic evidence suggests the connection of film structure with internal structure, in the remaining rocks such connection is not proved.

Incidentally, the study throws some interesting light on the structure of Egyptian flints, and the importance of microcline felspars in the group of granites examined may be emphasized.

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#### APPENDIX II.

While the present pamphlet was in the press a note on the Aswan Cataract was published by M. R. Fourtau. (1)

M. Fourtau quotes the observation of M. Jean Brunhes that the surface of the rocks at the cataract is covered "en général d'une sorte de vernis noir qui les fait luire au soleil comme des masses de métal poli" (2), and M. Brunhes' opinion that the film is simply "une couche d'altération" is also quoted.

The description of the film by Lortet et Hugounenq and their explanation of its composition and formation already referred to are also mentioned.

Of the theory advanced by Lortet et Hugounenq to explain the formation of the film, M. Fourtau writes: "L'Hypothèse est ingénieuse mais ne répond pas selon moi à la réalité des faits.

M. Fourtau then proceeds to give his own explanation of the phenomenon. Reasoning by analogy from the results obtained by Daubrée (3) on the decomposition of silicates contained in a revolving iron cylinder, M. Fourtau concludes — apparently without any analyses — that the film consists of silicates of iron and manganese formed in the same manner as the silicate of iron in Daubrée's cylinder, that is, by the decomposition of the felspar and the separation in the first instance of alkaline silicates, which subsequently attack the iron and manganese in the rock forming the respective silicates.

M. Fourtau writes: "au fur et à mesure que les cristaux de feldspath et de hornblende se décomposaient sous l'action énergique du courant, ils mettaient à découvert les particules si fines de peroxyde de fer et d'oxyde de manganèse qui, comme nous le montrent les coupes minces, entourent ces cristaux, et il s'est formé un silicate de fer et de manganèse insoluble et indécomposable dans les mêmes conditions que le feldspath."

Even from a microscopic examination of sections of the Aswan rocks there is no evidence that the crystals of felspar are surrounded by the oxides of iron and manganese in fine particles in the manner stated. In some cases crystals of haematite and magnetite certainly occur, but in the felspars these are usually found along cracks or scattered in the

(1) La cataracte d'Assouan. By R. Fourtau. Bulletin de la Société Khédiviale de Géographie VI Série, N° 7, Le Caire, 1905.

(2) La Tactique des Tourbillons. By J. Brunhes. Mémoires de la Société Fribourgeoise des Sciences-naturelles.

(3) Daubrée. Études synthétiques.

interior of the crystals, while there is no proof that the manganese is ever present as oxide, this substance in all probability existing already in the form of silicate.

Unfortunately therefore for M. Fourtau's hypothesis the conditions in the river are neither identical with those in Daubrée's cylinder, nor so simple as imagined.

Further, from the analyses of the film made in this laboratory, the iron and manganese are present in too large an amount to be combined entirely with the silica, and the film also contains various other substances such as lime, magnesia, phosphoric acid, etc., the presence of which the theory leaves unexplained.

M. Fourtau's explanation also completely fails to account for the film existing on sandstone or limestone, for in these cases it certainly could not have been formed in the manner suggested.

M. Fourtau gives some evidence of the occurrence of the film below low water level; he writes: "Je pouvais en dire autant de toutes les traces d'exploitation dans le lit du fleuve.

"Partout où l'on a enlevé la roche la cicatrice reste rose, et dans certain endroits l'on voit aussi sur la roche la ligne des coins se détacher sur le fond noir du rocher."

On this point of occurrence or non-occurrence of the film below low water level, Mr. M. Macdonald, the Director of the Aswan Reservoir, writes: (1) "I was suddenly reminded of your quest for evidence of 'polishing' or 'blackening' of the rock surface in the Cataract below low water line by observing a number of dead oyster shells sticking to very highly 'polished' rock in the excavation we are making for aprons down stream of the Dam. I examined for further evidence and found it in abundance all around at depths not less than 3 metres below low water.

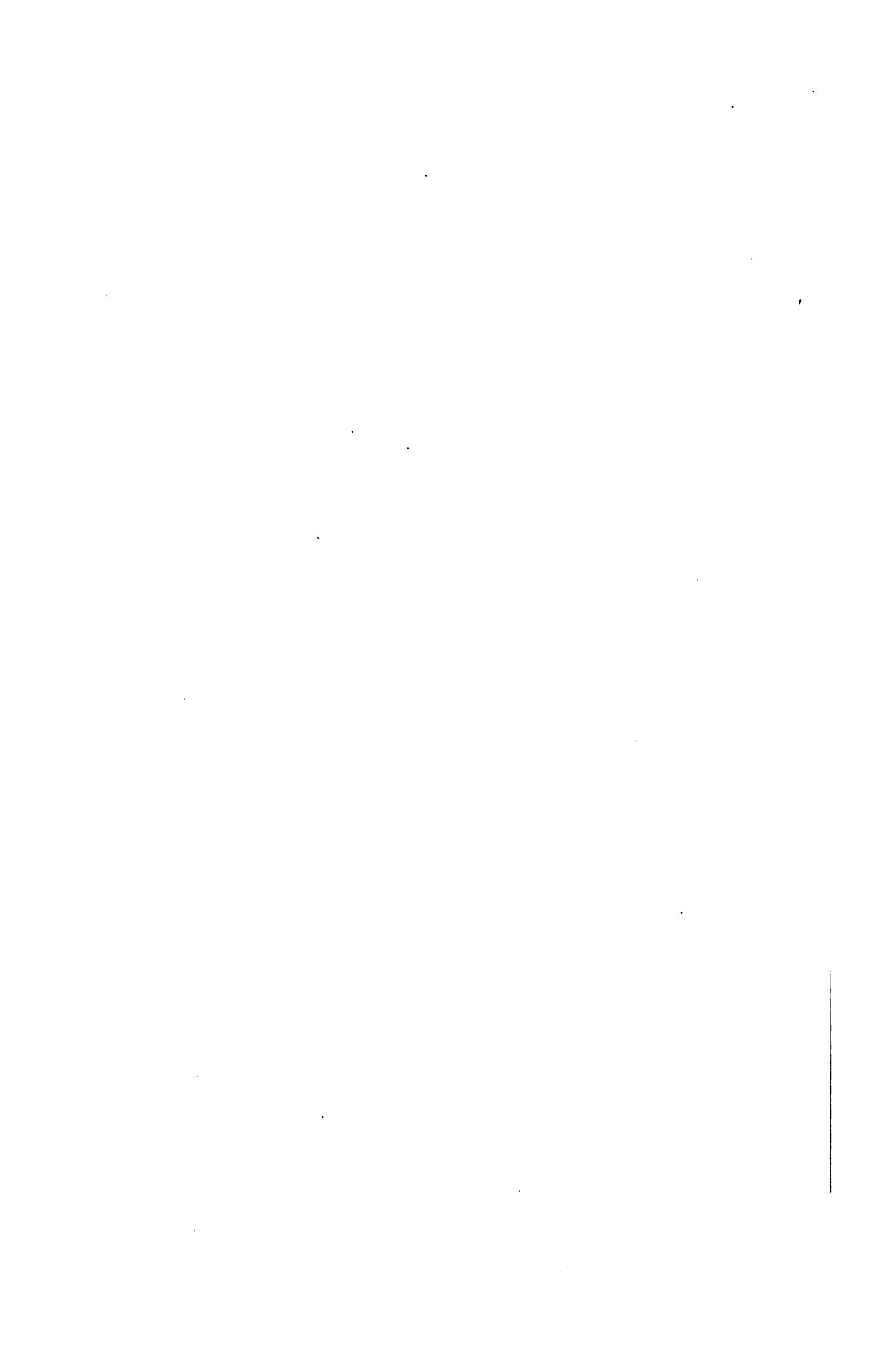
"As the water is phenomenally low this year and I had occasion to be near the Islands opposite the Cataract Hotel, I looked for evidence there and found the polishing right down to water line, a line which has only been reached once before in 150 years, and every indication that it went below that point".

In a second letter Mr. Macdonald writes: "the blackening occurs below low water line."

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(1) Private letter, April, 1905.

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